

FORM PTO-1390 (REV. 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 1-15467
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 CFR 1.5) 09/890413
INTERNATIONAL APPLICATION NO. PCT/GB00/00402	INTERNATIONAL FILING DATE 10 February 2000 (10.02.00)	PRIORITY DATE CLAIMED 12 February 1999 (12.02.99)	
TITLE OF INVENTION IMPROVEMENTS IN COATING GLASS			
APPLICANT(S) FOR DO/EO/US JOHN ROBERT SIDDLE			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). executed - three pages 10. <input type="checkbox"/> An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 			
Items 11 to 20 below concern document(s) or information included:			
<ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included with PTO-1595 (four pages) 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 14. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 15. <input type="checkbox"/> A substitute specification. 16. <input type="checkbox"/> A change of power of attorney and/or address letter. 17. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 18. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 19. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 20. <input checked="" type="checkbox"/> Other items or information: return card, express mail certificate, copies of the cover page of the published international application, PCT/ISA/210 International Search Report and International Preliminary Examination Report IPEA/409; 			

U.S. APPLICATION NO. 09/890413 <small>(Information, see 37 CFR 1.53)</small>		INTERNATIONAL APPLICATION NO. PCT/GB00/00402		ATTORNEY'S DOCKET NUMBER 1-15467	
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21. <input checked="" type="checkbox"/> The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO..... \$1000.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
				\$ 860.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(e)).				\$ -	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	\$	
Total claims	25 - 20 =	5	x \$18.00	\$ 90.00	
Independent claims	4 - 3 =	1	x \$80.00	\$ 80.00	
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$270.00	
TOTAL OF ABOVE CALCULATIONS =				\$ 1,030.00	
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2.				+ \$ -	
SUBTOTAL =				\$ 1,030.00	
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				\$ -	
TOTAL NATIONAL FEE =				\$ 1,030.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +				\$ 40.00	
TOTAL FEES ENCLOSED =				\$ 1,070.00	
				Amount to be refunded: \$	
				charged: \$	

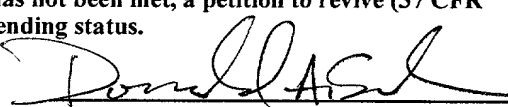
a. ☒ A check in the amount of \$ 1,070.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. _____ in the amount of \$ _____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any
 overpayment to Deposit Account No. 13-1816. ~~A duplicate copy of this sheet is enclosed.~~

d. ☐ Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card
 information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR
 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

SEND ALL CORRESPONDENCE TO: MARSHALL & MELHORN, LLC Donald A. Schurr Four SeaGate - 8th Floor Toledo, Ohio 43604 Phone: (419) 249-7145 Fax: (419) 249-7151 July 30, 2001	 SIGNATURE <u>DONALD A. SCHURR</u> NAME <u>34,247</u> REGISTRATION NUMBER
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I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on July 30, 2001 and is addressed to the Commissioner for Patents, Box PCT, Washington, D.C. 20231.

Kathleen J. Moore
(signature of person mailing correspondence)

Kathleen J. Moore

(Typed name of person mailing correspondence)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:]
JOHN ROBERT SIDDLE] Group Art Unit:
Serial No.]
Filed:] Examiner:
Filing Under 35 U.S.C. 371 in]
the DO/EO/US off PCT/GB00/00402]
filed 10 February 2000] Attorney Docket 1-15467
For: IMPROVEMENTS IN COATING GLASS]

July 30, 2001

Box PCT
Commissioner for Patents
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Honorable Sir:

Prior to the first Office Action and before calculating the filing fee, please amend the application being filed concurrently herewith under 35 U.S.C. 371 as follows:

IN THE CLAIMS

Please amend original claims 3, 4, 7, 8, 11, 12, 14, 15, 17, 18, 20 and 21 as follows:

3. (Amended) A process as claimed in claim 1 wherein each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom of oxygen.
4. (Amended) A process as claimed in claim 1 wherein the gaseous oxygen scavenger is a hydrocarbon.
7. (Amended) A process as claimed in claim 1 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that is sufficient to alleviate oxidation and/or degradation of the reflective metal layer.
8. (Amended) A process as claimed in claim 1 wherein the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen.
11. (Amended) A process as claimed in claim 1 wherein the reflective metal layer is a silver layer.

12. (Amended) A process as claimed in claim 1 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.
14. (Amended) A process as claimed in claim 1 wherein the sheet resistance of the reflective metal layer is below 12 Ω /square.
15. (Amended) A process as claimed in claim 1 wherein the coating atmosphere contains a measurable amount of oxygen and the sheet resistance of the reflective metal layer deposited in the coating atmosphere is below 12 Ω /square.
17. (Amended) A process as claimed in claim 1 wherein the low pressure deposition process for depositing the reflective metal layer is sputtering.
18. (Amended) A process for production of a coated substrate as claimed in claim 1 that additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer.

20. (Amended) A process as claimed in claim 1 wherein the substrate is curved.
21. (Amended) Coated glass produced by a process as claimed in claim 1.

Please add the following new claims:

24. (New) A process as claimed in claim 19 wherein the substrate is curved.
25. (New) Coated glass produced by a process as claimed in claim 19.

REMARKS

Applicant has amended the claims to eliminate multiple dependencies and adapt the claims to U.S. patent practice. A separate marked up copy of the amended claims is attached hereto entitled "Version With Markings To Show Changes Made".

Claims 3, 4, 7, 8, 11, 12, 14, 15, 17, 18, 20 and 21 have been amended. New claims 24 and 25 have been added. Claims 1-25 are currently pending in the present application. No new matter has been added by any of these amendments.

Favorable consideration of the application as amended is respectfully requested.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Donald A. Schurr", written over a horizontal line.

Donald A. Schurr

Registration No. 34,247

ATTORNEYS

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Version With Markings To Show Changes Made

3. (Amended) A process as claimed in claim 1 [or claim 2] wherein each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom of oxygen.
4. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the gaseous oxygen scavenger is a hydrocarbon.
7. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that is sufficient to alleviate oxidation and/or degradation of the reflective metal layer.
8. (Amended) A process as claimed in [one of the preceding claims] claim 1 wherein the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen.

11. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the reflective metal layer is a silver layer.
12. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.
14. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the sheet resistance of the reflective metal layer is below 12 Ω /square.
15. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the coating atmosphere contains a measurable amount of oxygen and the sheet resistance of the reflective metal layer deposited in the coating atmosphere is below 12 Ω /square.
17. (Amended) A process as claimed in [the preceding claims] claim 1 herein the low pressure deposition process for depositing the reflective metal layer is sputtering.

18. (Amended) A process for production of a coated substrate as claimed in [any one of the preceding claims] claim 1 that additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer.
20. (Amended) A process as claimed in [any one of the preceding claims] claim 1 wherein the substrate is curved.
21. (Amended) Coated glass produced by a process as claimed in claim 1 [any one of the preceding claims].

Improvements in Coating Glass

This invention relates to a process for the production of a coated substrate and, in particular, it relates to a process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process.

Substrates coated with a reflective metal layer, typically silver 5 nm to 30 nm thick, may be produced with low emissivity and a high visible light transmission i.e. reflecting a high proportion of infra-red radiation incident upon them but allowing visible radiation to pass through. For optimum light transmission the silver layers are sandwiched between anti-reflection layers usually of metal oxide. The use of such coatings on window glass leads to a reduction in heat loss. Substrates having such coatings are described, for example, in UK patent specification GB 2 129 831.

Coatings having multiple (usually two) silver layers, each silver layer being sandwiched between anti-reflection layers, may also be produced. Coatings with multiple silver layers have both low emissivity, and with appropriate layer thicknesses, a low transmission of solar heat.

Coatings with silver layers are produced by deposition processes in a coating atmosphere at low

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pressure, especially by sequential deposition of a metal oxide anti-reflection layer, a silver layer, and a metal oxide anti-reflection layer. The metal oxide layers are usually deposited by reactive sputtering in a coating atmosphere containing oxygen and an inert gas (usually argon). Silver and other reflective metal layers are deposited by sputtering in an inert gas (usually argon). In US patent specification 5,837,361 a process for the production of a coating having layers of bismuth oxide (Bi_2O_3), zinc oxide, silver, nichrome, tin oxide and bismuth oxide is described, the metal oxide layers being reactively sputtered in an argon atmosphere containing oxygen and the silver layer being sputtered in an argon atmosphere with the addition of 5% by volume hydrogen.

In commercial production of sputtered coatings, sputtering of each layer usually proceeds in a sputtering chamber that has been initially evacuated to high vacuum (usually of about 10^{-6} mbar) and then raised to an operating pressure of around 10^{-3} mbar by flowing the gases making up the coating atmosphere into the chamber. The operating pressure is low so that the path length of the coating species sputtered from the target is high enough to reduce scattering and thereby maintain the efficiency of the coating process. Deposition of coatings may be performed in a single chamber having a readily changeable atmosphere or multiple, serially connected deposition chambers each containing the

desired atmosphere. In the multiple chamber case, the substrate is moved sequentially between the chambers, which are separated by gas-tight slit valves to alleviate leakage of the coating atmosphere between chambers. It is particularly important to alleviate leakage of oxygen from the metal oxide deposition chambers to the silver deposition chambers because the reflective metal layer oxidises or degrades if deposited in a coating atmosphere containing oxygen. To reduce leakage further there are usually additional chambers, positioned between the deposition chambers, which are pumped at high rates so that oxygen in the coating atmospheres used for sputtering metal oxide layers is removed before it can leak into the silver deposition chamber.

The need for high pumping rates in the deposition chambers and in the additional chambers requires expensively high pumping capacity, slows production rates considerably and leakage can still occur. Particular problems arise where the substrate to be coated is curved. In order to accommodate the greater cross-section of curved substrates, high clearance slit valves are required with an increased likelihood of leakage and in consequence a need for even higher pumping rates.

We have discovered that a low pressure deposition process for depositing a reflective metal layer can

tolerate the presence of oxygen if a gaseous oxygen scavenger is present in the coating atmosphere.

The present invention accordingly provides a process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere, characterised in that the coating atmosphere contains a gaseous oxygen scavenger, wherein when the reflective metal layer is deposited as a layer in a multilayer coating which also contains a bismuth oxide layer said gaseous oxygen scavenger is not hydrogen.

In a preferred aspect, the present invention provides a process for the production of a coated substrate, characterised in that the coating atmosphere contains a gaseous oxygen scavenger other than hydrogen.

Oxygen can be present at a level that is too low to conveniently measure but nevertheless is high enough to oxidise or degrade the reflective metal layer. Thus, the coating atmosphere may contain the oxygen scavenger as a preventative measure, even if the deposition process is performed in a coating atmosphere that contains no measurable amount of oxygen.

Usually, the deposition process is performed in a coating atmosphere that contains oxygen (i.e. that contains a measurable amount of oxygen). The presence of oxygen in the coating atmosphere may arise by leakage from a deposition chamber containing a second coating

atmosphere that contains oxygen or from outside (e.g. from the air).

The gaseous oxygen scavenger may be any substance capable of combining chemically with oxygen under the conditions of the low pressure deposition process. Such combination may take place in the gas phase or on the surface of the substrate.

Preferably each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom or more preferably with more than one molecule of oxygen. This is advantageous because then only a small amount of oxygen scavenger need be added to the first coating atmosphere. Adding a large amount of oxygen scavenger to the atmosphere may increase the pressure and therefore reduce the efficiency of deposition. Preferably the gaseous oxygen scavenger has a relatively high vapour pressure at room temperature.

It is advantageous if the gaseous oxygen scavenger is such that the products of its interaction with the surface of the reflective metal layer or of its combination with oxygen are themselves gaseous because the likelihood of solids contamination of the reflective metal layer is thereby reduced. A preferred oxygen scavenger is a hydrocarbon (for example an alkane, alkene, or alkyne), more preferably a C_1 to C_4 hydrocarbon (for example ethane, ethylene, acetylene, propane or butane) and most preferably methane. Oxygen

Preferably, the reflective metal layer is deposited in a coating atmosphere comprising a flowing gaseous mixture and wherein the gaseous oxygen scavenger is introduced into the coating atmosphere by incorporation in the flowing gaseous mixture.

The amount of oxygen scavenger in the coating atmosphere should not be so great as to unacceptably increase the pressure, but should be sufficient to alleviate oxidation or degradation of the reflective metal layer. In practice, if the quality of the reflective metal coating deteriorates during deposition (the deterioration is determined, for example, by an increase in sheet resistance), the amount of oxygen scavenger in the coating atmosphere would be increased to reverse, alleviate or prevent the deterioration.

Thus, preferably, the coating atmosphere contains the gaseous oxygen scavenger in an amount that is

sufficient to alleviate oxidation and/or degradation of the reflective metal layer.

Usually the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen, preferably that exceeds 30 mol% of the amount of oxygen, and more preferably that exceeds 50 mol%, of the amount of oxygen.

Preferably, the reflective metal layer is a silver layer, and preferably the reflective metal layer has a thickness in the range 5 to 30 nm, more preferably in the range 7 to 18 nm. At thicknesses lower than about 5 nm the reflective metal layer may be discontinuous (this results from the growth mechanism of a layer and may occur even on a flat substrate) and will then not possess the properties of the bulk metal resulting in poor infra red reflecting properties. Thicknesses higher than about 30 nm may cause the coated glass to have too high a visible light reflectivity.

It is known to estimate the infra red reflection of reflective metal layers by measuring the sheet resistance of the coating. A high sheet resistance indicates poor infra red reflecting properties (i.e. high emissivity), whereas a low sheet resistance indicates good infra red reflecting properties (i.e. low emissivity). Oxidation or oxygen induced degradation of a reflective metal layer increases the sheet resistance

with consequently poorer infra red reflecting properties. The sheet resistance of a layer is defined as:

$$R_s = \rho / d$$

where ρ is the resistivity of the layer, and d is its physical thickness (see, for example, *Thin Film Technology*, R.W. Berry, P.M. Hall and M.T. Harris (D. Van Nostrand, 1968) pp 329-331). The units of sheet resistance are Ω/square .

In the present invention, preferably the sheet resistance of the reflective metal layer is below 12 Ω/square . It is advantageous if, in the process, the coating atmosphere contains a measurable amount of oxygen and the sheet resistance of the reflective metal layer deposited in a first coating atmosphere containing oxygen is below 12 Ω/square , preferably below about 8 Ω/square .

In a preferred embodiment, the process additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer. The metal oxide layer will usually be deposited from a coating atmosphere that contains oxygen. Usually, at least two metal oxide anti-reflection layers will be deposited so that the reflective metal layer is sandwiched between metal oxide anti-reflection layers. When two or more reflective metal layers are deposited (e.g. to provide a coating

with low solar heat transmission) each reflective metal layer will usually be sandwiched between metal oxide anti-reflection layers. Examples of metal oxides suitable for use as anti-reflection layers include: zinc oxide, tin oxide, silicon oxide, zirconium oxide, titanium oxide, niobium oxide, molybdenum oxide, tungsten oxide, silicon nitride, silicon oxynitride and silicon oxycarbide. Additional layers of metal oxide, metals (e.g. nichrome, inconel or titanium) or other materials may also be present in the multi-layer coating by, for example, being deposited between the metal oxide anti-reflection layers and the reflective metal layers and/or between the substrate and a metal oxide layer.

Low pressure deposition processes are performed in flowing gas at pressures of below about 10^{-1} mbar, or preferably lower and include such processes as sputtering, reactive sputtering, evaporation and other forms of physical vapour deposition. The preferred low pressure deposition process for depositing the reflective metal layer is sputtering.

In prior art processes, deposition of each layer usually proceeds in a sputtering chamber, which has been initially evacuated to about 10^{-6} mbar to ensure removal of air, especially oxygen. The pressure of the chamber is then raised to an operating pressure of approximately 10^{-3} mbar by injection of the gases making up the coating atmosphere (usually argon for sputtering of the

reflective metal and a mixture of argon and oxygen for sputtering of metal oxides).

The present invention is of particular benefit because with a gaseous oxygen scavenger present in the coating atmosphere, the deposition process is better able to tolerate incomplete removal of air.

Thus, in one embodiment, the present invention additionally provides a low pressure process for the deposition of a reflective metal layer on a substrate, performed in a deposition chamber containing a coating atmosphere, comprising evacuating the deposition chamber to a low first pressure, introducing a coating gas into the deposition chamber thereby raising the pressure therein to a higher second pressure of about 10^{-3} mbar, and sputtering the reflective metal layer at the second pressure, characterised in that the first pressure is about 10^{-4} mbar and in that the coating atmosphere contains a gaseous oxygen scavenger.

This is advantageous because evacuating to a higher pressure is more easily, rapidly and cheaply achieved (particularly because a lower pumping capacity is required).

The substrate to be coated is preferably glass but may be, for example, a transparent plastics substrate. The substrate may be flat or curved.

Coated glass produced by a process according to the invention has uses in many areas of glass use including

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in multiple glazing units and in laminated glass. Thus, in a further aspect the present invention provides coated glass comprising a glass substrate and a multilayer coating deposited on a surface of the glass substrate, wherein said multilayer coating comprises, in sequence, a first metal oxide anti-reflection layer, a reflective metal layer and a second metal oxide anti-reflection layer, characterised in that the reflective metal layer is deposited by a low pressure deposition process performed in a coating atmosphere containing a gaseous oxygen scavenger other than hydrogen.

In a further embodiment, the present invention provides use of a gaseous oxygen scavenger to reduce oxidation or oxygen induced degradation of a reflective metal layer in a process for the production of a coated substrate, said process comprising depositing the reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere containing the oxygen scavenger.

The invention is illustrated by the following Examples in which silver reflective metal layers were deposited on glass substrates by sputtering in a coating atmosphere containing argon, oxygen to simulate oxygen leakage and methane as gaseous oxygen scavenger.

Examples 1-5

Layers of silver were deposited on soda-lime glass substrates (of dimension 20 x 20 cm, 20 x 10 cm or 20 x 40 cm) at room temperature and at a pressure of 2×10^{-3} mbar by DC magnetron sputtering using a silver target of 99.9% purity and a power density (over approximately 160 cm²) of about 3.1 W/cm². The coating atmosphere consisted of argon, oxygen and methane. All gases were obtained from B.O.C. Ltd and were Zero grade.

The glass substrates were positioned vertically in a holder and advanced at a glass traversal speed of 10-35 cm/min through the sputtering zone with a coating aperture of dimension approximately 1 cm.

After coating, the thickness of the silver layer was measured by computer fitting the optical transmission and reflection spectra of the coated glass, the spectra having been determined using a Hitachi U400 spectrophotometer.

The sheet resistance (in ohm/square) of the silver coatings was determined by a non-contact conductance monitor (Delcon Instruments 717 Conductance monitor).

Table 1 describes, for Examples 1-5, the flow rates of the gases in the coating atmosphere (in standard cm³ per minute), the glass traversal speed, the thickness of the silver layer as determined and the sheet resistance of the coated glass.

Comparative Examples A and B

Comparative Example A was conducted under the same conditions as Example 1 except that no oxygen and no methane were present in the coating atmosphere.

Comparative Example B was also conducted under the same conditions as Example 1 except that no methane was present in the coating atmosphere.

Table 2 describes, for Comparative Examples A and B, the flow rates of the gases in the coating atmosphere, (in standard cm³/min), the glass traversal speed, the thickness of the silver layer and the sheet resistance of the coated glass.

Table 1

Example	Flow rates of gases (standard cm ³ /min)			Glass traversal speed (cm/min)	Thickness of silver layer (nm)	Sheet resistance (Ω/square)
	Ar	O ₂	CH ₄			
1	22	4	6	35	7.3	8.1
2	22	4	6	25	11.6	5.3
3	22	4	0.6	35	9.2	12.0
4	22	40	20	20	8.7	11.9
5	22	40	30	10	15	3.8

Table 2

Comparative Example	Flow rates of gases (standard cm ³ /min)			Glass traversal speed (cm/min)	Thickness of silver layer (nm)	Sheet resistance (Ω/square)
	Ar	O ₂	CH ₄			
A	22	-	-	35	9.2	5.0
B	22	4	-	35	9.2	12.5

Claims

1. A process for the production of a coated substrate comprising depositing a reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere, characterised in that the coating atmosphere contains a gaseous oxygen scavenger, wherein when the reflective metal layer is deposited as a layer in a multilayer coating which also contains a bismuth oxide layer, said gaseous oxygen scavenger is not hydrogen.
2. A process as claimed in claim 1 wherein the process is characterised in that the coating atmosphere contains a gaseous oxygen scavenger other than hydrogen.
3. A process as claimed in claim 1 or claim 2 wherein each molecule of the gaseous oxygen scavenger is capable of combining with more than one atom of oxygen.
4. A process as claimed in any one of the preceding claims wherein the gaseous oxygen scavenger is a hydrocarbon.

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5. A process as claimed in claim 4 wherein the gaseous oxygen scavenger is a C₁ to C₄ hydrocarbon.
6. A process as claimed in claim 5 wherein the gaseous oxygen scavenger is methane.
7. A process as claimed in any one of the preceding claims wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that is sufficient to alleviate oxidation and/or degradation of the reflective metal layer.
8. A process as claimed in one of the preceding claims wherein the coating atmosphere contains a measurable amount of oxygen and contains the gaseous oxygen scavenger in an amount that exceeds 15 mol% of the amount of oxygen.
9. A process as claimed in claim 8 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that exceeds 30 mol% of the amount of oxygen.
10. A process as claimed in claim 9 wherein the coating atmosphere contains the gaseous oxygen scavenger in an amount that exceeds 50 mol% of the amount of oxygen.

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17. A process as claimed in the preceding claims wherein the low pressure deposition process for depositing the reflective metal layer is sputtering.
18. A process for production of a coated substrate as claimed in any one of the preceding claims that additionally comprises depositing a metal oxide anti-reflection layer by a low pressure deposition process before depositing the reflective metal layer.
19. A low pressure process for the deposition of a reflective metal layer on a substrate, performed in a deposition chamber containing a coating atmosphere, comprising evacuating the deposition chamber to a low first pressure, introducing a coating gas into the deposition chamber thereby raising the pressure therein to a higher second pressure of about 10^{-3} mbar, and sputtering the reflective metal layer at the second pressure, characterised in that the first pressure is about 10^{-4} mbar and in that the coating atmosphere contains a gaseous oxygen scavenger.
20. A process as claimed in any one of the preceding claims wherein the substrate is curved.

21. Coated glass produced by a process as claimed in any one of the preceding claims.
22. Coated glass comprising a glass substrate and a multilayer coating deposited on a surface of the glass substrate, wherein said multilayer coating comprises, in sequence, a first metal oxide anti-reflection layer, a reflective metal layer and a second metal oxide anti-reflection layer, characterised in that the reflective metal layer is deposited by a low pressure deposition process performed in a coating atmosphere containing a gaseous oxygen scavenger other than hydrogen.
23. Use of a gaseous oxygen scavenger to reduce oxidation or oxygen induced degradation of a reflective metal layer in a process for the production of a coated substrate, said process comprising depositing the reflective metal layer on to a substrate by a low pressure deposition process performed in a coating atmosphere containing the oxygen scavenger.

ABSTRACTImprovements in Coating Glass

A process for the production of a coated substrate, preferably glass, comprising depositing a reflective metal, especially a silver, layer by a low pressure deposition process performed in a coating atmosphere that contains a gaseous oxygen scavenger. The presence of the gaseous oxygen scavenger alleviates oxidation of the silver layer by any oxygen gas present in the coating atmosphere. The gaseous oxygen scavenger may be a hydrocarbon and is preferably methane. The coating process is preferably sputtering.

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COMBINED DECLARATION AND POWER OF ATTORNEY
IN ORIGINAL APPLICATION

ATTORNEY DOCKET
NO. 1-15467

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name,

I believe that I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

IMPROVEMENTS IN COATING GLASS

the specification of which

XX is attached hereto

— was filed on _____
as U.S. Serial No. _____
and was amended on _____.

XX filing under 35 U.S.C. 371 off PCT Int'l Appln.
No. PCT/GB00/00402 (Filed 10 February 2000)

hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

XX and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent; and

— if this is a continuation-in-part application, information that occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application, in accordance with 37 CFR 1.63(e); and

— in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)			Priority Claimed	
<u>99/03056.1</u>	<u>UNITED KINGDOM</u>	<u>12 February 1999</u>	<u>X</u>	
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No
<u> </u>	<u> </u>	<u> </u>	<u> </u>	<u> </u>
(Number)	(Country)	(Day/Month/Year Filed)	Yes	No

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

<u>PCT/GB00/00402</u>	<u>10 February 2000</u>	<u>PENDING</u>
(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)
<u> </u>	<u> </u>	<u> </u>
(Appln. Serial No.)	(Filing Date)	(Status)
		(patented, pending, abandoned)

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith with full power of substitution and revocation: Phillip S. Oberlin, Reg. No. 19,066; D. Edward Dolgorukov, Reg. No. 26,266; Donald A. Schurr, Reg. No. 34,247; Mark A. Hixon, Reg. No. 44,766; Stephen P. Evans, Reg. No. 47,281; and Angelica M. Colwell, Reg. No. 46,637. Address all telephone calls to: Donald A. Schurr at telephone number (419) 249-7145. Address all correspondence to MARSHALL & MELHORN, LLC, Four Seagate - 8th Floor, Toledo, Ohio 43604, Attention: Donald A. Schurr.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Inventor's signature John Robert Siddle Date 25th June 2001
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Full name of third joint inventor, if any _____

Third Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____

Full name of fourth joint inventor, if any _____

Fourth Inventor's signature _____ Date _____

Residence _____

Citizenship _____ Post Office Address _____